STSM Cost Action FP1405: Production of biodegradable packaging by 3D printing

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Host institution: PFI part of RISE, Trondheim (Norway)
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Introduction

During the last years environmental concern has motivated several political and industrial initiatives towards production of environmentally sound and sustainable materials. Hence, several major companies have developed social responsibility strategies, with clear environmental focus. Consequently, the biocomposites science community is nowadays very interested in the development of environmentally friendly materials. Their properties, such as, low density, nontoxic, low cost, more environmentally friendly properties, making them candidates for multitude of applications [1,2]. The main advantage of these biocomposites is that natural fibers are easily obtained from renewable resources. The resulting biocomposites offer the possibility to manufacture products relatively easy with good properties, contributing to reduce potential environmental problems [3].

However, the use of biocomposite materials with natural fibers and classic plastic polymers did not solve completely the environmental problem associated with the use of fossil-based materials (Polypropylene, Polyethylene, etc.). Usually, a range of plastic polymer substitution by natural fiber addition was found between 10 to 50 % w/w [4,5]. It means that at least the 50 % w/w of biocomposite material is fossil-based. In this sense, the use of bioplastics could help to improve the environmental character of future plastic products. Nowadays, the production of bioplastics is expensive [6]. Addition of natural fibers would be highly beneficial from the point of view of price and mechanical properties.

However, the use of natural fibers have some disadvantages, such as the limited processing temperatures below 220 ºC (Yang et al. 2005) and the incompatibility between hydrophilic fibers and commonly hydrophobic polymer matrix. The use of maleated polyethylene as coupling agent is a rather attractive method because it avoid the use of expensive and toxic methods [8]. The improvement of the interface between fibers and matrix can lead to optimized physical and mechanical properties of the biocomposite material [9].

In this work, thermomechanical pulp (TMP) fibers from softwood were used as reinforcement of BioPE. Biocomposites containing TMP fibers from 10 to 30 % were formulated and prepared. Furthermore, the obtained biocomposites was used for filament extrusion. Finally, the 3D printability of biocomposite filaments was tested for future biobased packaging materials.

Materials and methods

Materials

Thermomechanical pulp fibers (TMP) in granule form, 8 mm of diameter were supplied by Norske Skog Saugbrugs (Norway). The TMP fibers collected from the reject press were granulated and dried by Norske Skog Saugbrugs.

The polymer matrixes were bio-polyethylene (BioPE SHD7255LSL) provided by Braskem (Sao Paulo, Brazil). In order to improve the compatibility between fibers and BioPE, polyethylene functionalized with maleic anhydre (MAPE) was used as a coupling agent (Fusabond MB100D, 0.9%) acquired from Eastman Chemical Products (San Roque, Spain).

Reagents used for fiber characterization were bought from Scharlab Spain (Barcelona, Spain) and used without further purification.

Methods

Biocomposite processing

TMP fibers, together with BioPE and MAPE, were mixed at different percentages (wt/wt) by using an intensive kinetic Gelimat mixer. Initially, the fiber amount was introduced at 300 rpm for its disaggregation. Then, BioPE together with coupling agent was added also at 300 rpm. Finally, the mixing process was carried out during 2 minutes at 3000 rpm and were discharged when approximately 210 ºC of temperature was reached. Biocomposite blends containing 10 to 20 wt. % of TMP with 0 to 6 wt. % of MAPE (with regard to the fiber content) were prepared. The obtained blends were cut down to small particle in the size range of 10 mm using a miller. The particles were dried and stored at 80ºC during 24h at least. The obtained biocompounds were used for injection-molding dogbones for mechanical characterization and for filament extrusion for 3D-printing.

Melt flow index characterization

The melt flow index (MFI) of the TMP mixtures were tested with a plastometer Ceast™ (Torino, Italy). The measurements were performed at 210 ºC with a load of 5 kg. Plastometer is equipped with two independent thermal resistances heating a capillary. The MFI value is the amount of biocomposite melted and delivered at constant temperature and load for 10 minutes.

Filament extrusion

Filament extrusion of BioPE and their biocomposites with TMP was performed using a mono screw extruder noztek xcalibur (United Kingdom). The extrusions were performed between 190 and 210 ºC, with a nozzle of 3 mm. The achievement of regular and correct diameter of filament by speed regulation becomes a key parameter for 3D printing process.

3D printing

3D printing of samples were performed with a 3D printer Original Prusa i3 mk2 (Prague, Czech Republic). Cube and dog bond samples were printed at 205 ºC.

Tensile tests

Test specimens were placed in a climatic chamber (Dycometal, Spain) at 50 % of relative humidity and 23 ºC during 48 hours at least before testing, according with ASTM D618.

Tensile properties of processed samples were studied using a Universal testing machine Instron TM 1122, with a 5 kN load cell. For a more precise deformations measurements an extensometer MFA2 was used. Tensile tests were carried out at a speed rate of 2 mm/min following ASTM D790 standard.

Preliminary results and discussion

Physical biocomposites properties

The melt flow index of resulting compounds is useful from a processing point of view. MFI permit evaluate the influence of natural fiber content on the processability by injection molding, extrusion or 3D-printing of TMP/BioPE biocomposites. The results of figure 1 shows the evolution of MFI when TMP fibers content was increased.

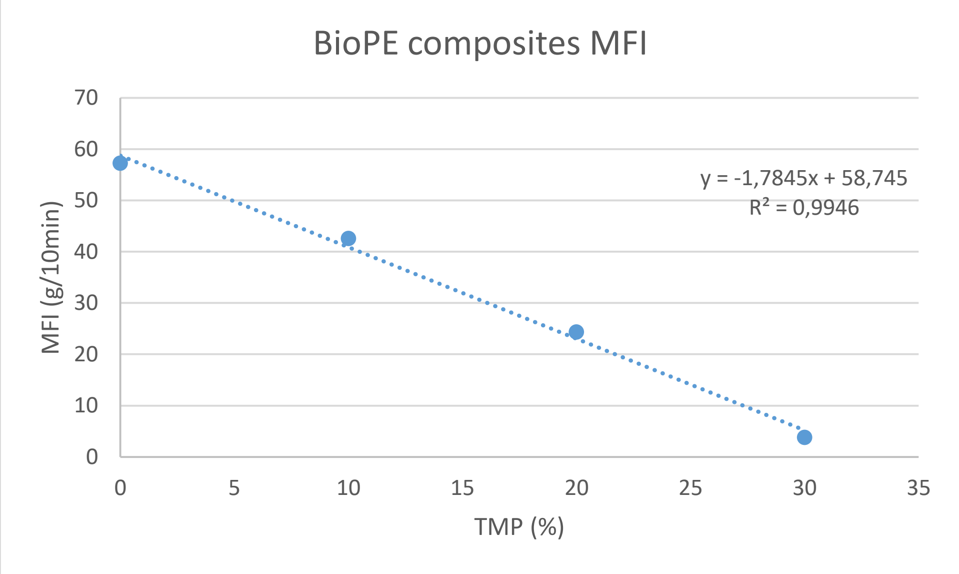

Figure 1. BioPE composites MFI front TMP amount

As it can be observed, results shows a notable decrease in MFI values as the TMP fibers content increases. This reduction of material fluidity implies some adjustments in pressure for injection molding and temperature and time of processing for extrusion or 3D-printing. This parameter limit the amount of natural fiber that could be added for a correct processing. The increase in viscosity of biocomposite materials when fiber content increase can be associated with the reduction of polymer chain mobility by its presence [10].

Filament extrusion

Filament extrusion of pure plastics and biocomposites were performed at different speed in order to obtain filaments with different diameters for each sample. In both cases, filaments with 30 % of TMP present high rigidity driving to a filament break when it was spooled. In figure 2, is shown one of the filaments obtained with BioPE and 10 % of TMP.

Figure 2. BioPE with 10 % of TMP filament.

The rigidity of this filaments with high content of fibers up to 20 % could be controlled by the addition of low amounts of PCL. The use of 5-10 % of PCL was shown as a useful method to reduce biocomposite rigidity.

Cube 3D print for printability assessment

In order to assess the 3D printability of biocomposites, initially cube samples was performed. As its possible to see in figure 3, 3D printing conditions were modified in order to obtain well defined cube.

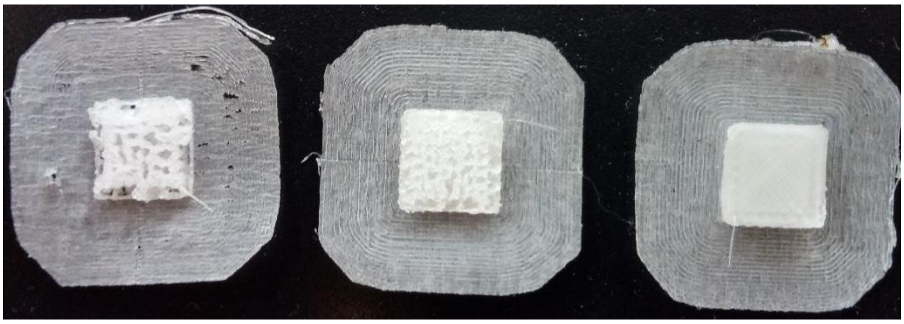

Figure 3. BioPE cube samples during 3D printing conditions determination.

In the same way, the 3D printing conditions of biocomposites needs to be adjusted again. In the figure 4 is shown the evolution of cube samples during this optimization of conditions.

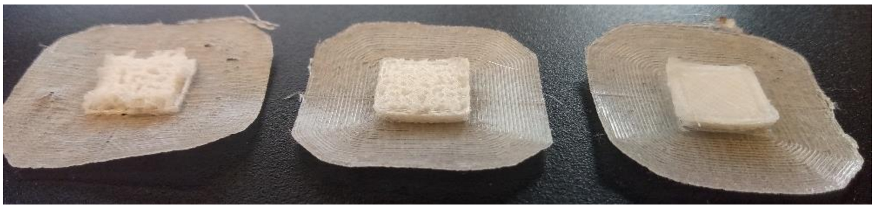

Figure 4. BioPE with 10% TMP cube samples during 3D printing conditions optimization.

Then, cube samples for each biocomposite was performed. Samples obtained (Figure 5), shown the feasibility of using biocomposites for 3D printing.

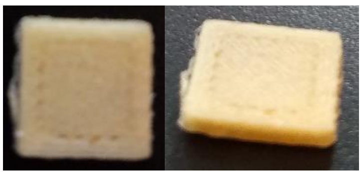

Figure 5. BioPE with 20% TMP cube samples

Interesting point is the visual cohesion of each sample, important for mechanical properties and also for consumers of future packaging materials. Contrary to the materials viscosities, the introduction of natural fibers in the bioplastic biocomposites promote better adhesion between different layers of 3D print.

Dog bonds samples 3D print

Finally, dog bonds samples for each material was produced for the mechanical characterization. As it's possible to see in the figure 6, the adhesion of material in the print surface is an important point for the correct printability.

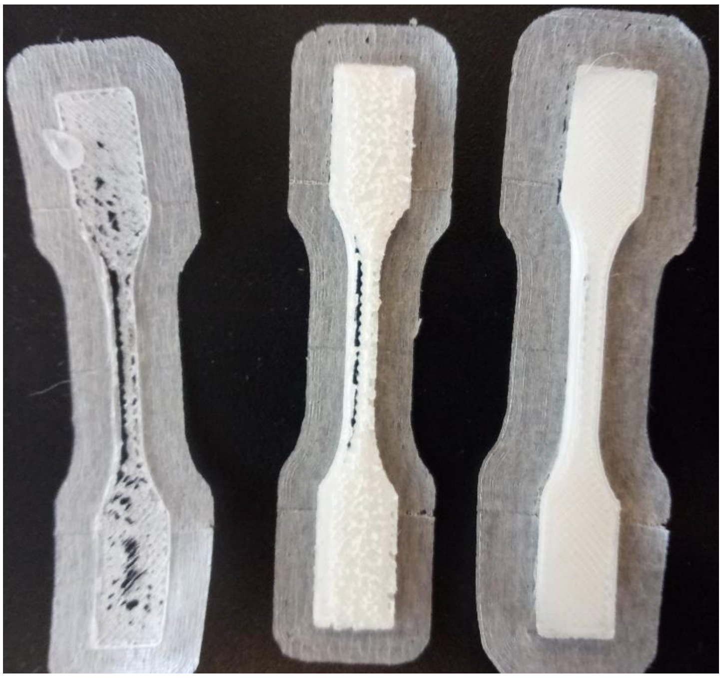

Figure 6. BioPE dog bond samples

Difficulties on adhesion of materials in the print surface was caused by the fast cooling of material during printing. In order to solve this problem, special tape was used on the heated printing bed. In this sense, a heating bed temperature between 30 and 50ºC was found as the best conditions.

Figure 7. BioPE with 20% of TMP dog bond samples

Again, when biocomposites with different amounts of TMP was printed, the high amounts of natural fibers in the biocomposites drive to higher adhesion between 3d print layers, figure 7.

Assessments in process

Currently, other tests listed below are under assessment:

1) Water uptake of samples.

2) Morphologic assessment of fibers after compounding by extraction.

3) Electronic microscopy of filaments and 3D printed samples.

4) Filaments mechanical testing: preliminary results show an important decrease on mechanical properties of filaments when they contain TMP fibers. This fact could be associated with an increased porosity in the filaments (determination by electronic microscopy).

5) Mechanical assessment of 3D printed samples, dog bonds. Preliminary tests show the increase on mechanical behavior when BioPEwas reinforced with TMP.

Conclusions

First conclusions of the STSM before the complete finishing of work were:

- Incorporation of TMP fibers increase the rigidity of the filaments and it limits the amount of natural fibers that is possible to add.
- The use of small amounts of PCL could be an interesting option to reduce the filament rigidity.
- Biocomposites of bioplastics with natural fibers are 3D printable.
- The addition of natural fibers on biobased plastics improve their mechanical behavior and also the addition between 3D printed layers.
- BioPE with TMP are interesting materials to substitute classic plastics on food packaging and to reduce the consumption of plastic from fossil resources.
- This STSM stablish a important collaboration between University of Girona and RISE-PFI, to work together in new advances on the food packaging materials using new technologies as 3D printing of reinforced biodegradable materials.

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